Synthesis of Magnetite Nanorods through Reduction of β-FeOOH

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Magnetite nanorods were fabricated by hydrothermal reduction of β-FeOOH nanorods at 160 °C for 20 h. X-ray diffraction (XRD), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and TEM were used to characterize structures and morphologies of the samples. On the basis of these methods, the growth mechanism was discussed. Also, the magnetic properties of the samples were characterized on a vibrating sample magnetometer (VSM).

It is well-known that the electronic, optical, and mechanical properties of nanoscaled materials behave quite diversely because of their different nanostructures. And it is the great differences that provide the possibility of producing nanodevices to be applied under various circumstances.[1] In recent years, considerable effort has been devoted to the design and controlled fabrication of materials with certain morphologies. Most of materials with relatively simple structures, such as oxides,[2,3] selenides,[4] metals, and alloys,[5] have been successfully synthesized. Magnetite, widely used as recording materials, catalyst, and so on, can also be expected to have unique magnetic properties as its nanostructure varies, and to have the potential applications as nanodevices. However, because of the complexity of its spinel structure, the morphology of magnetite is quite difficult to be controlled. To our best knowledge, only a few papers are related, among which surfactant-assisted synthesis,[6,7] magnetic field induced growth,[8] and ultrasound irradiation[9] are the main methods.

Since it is relatively difficult to directly synthesize magnetite with certain nanostructures, an indirect way is considered. It is reported that β-FeOOH, a kind of ferric oxyhydroxides, could be easily synthesized with different shapes.[10–12] If the shapes can be maintained when it is reduced, magnetite with different morphologies would be gained through controlling morphologies of β-FeOOH. In view of this, β-FeOOH nanorods were synthesized firstly, and then they were reduced to magnetite with hydrazine hydrate as the reductant.

$FeCl_3 \cdot 6H_2O$, NaOH, $N_2H_4 \cdot H_2O$ (85%), and CTAB, of analytical grade, were used in our experiments. The precursor, β-FeOOH, was prepared firstly. 4 mmol of $FeCl_3 \cdot 6H_2O$ and 1.0 g of CTAB were dissolved in 40 mL of double distilled water and magnetically stirred to form a homogeneous solution. Then it was transferred into a Teflon-lined stainless steel autoclave, kept at 80 °C for 12 h and cooled to room temperature on standing. The resulted yellow product, β-FeOOH, was reserved while the solution was poured. Following this was the addition of 40 mL of distilled water and magnetic stirring, then the addition of 1.6 g of NaOH and 2.0 mL of $N_2H_4 \cdot H_2O$. The autoclave was sealed again and kept at 160 °C for another 20 h. After the reaction finished, the black product was washed several times with distilled water and finally dried at 60 °C. The structure of the sample was examined by XRD using a Japan Rigaku D/maxγrA diffractometer with Cu Kα_1 radiation ($\lambda = 1.5408$ Å), while the morphology was detected by TEM (Hitachi H-800). Compositional analysis was carried on an ICP-AES. Room temperature M–H loops were measured on a VSM, BHV-55 up to $H = 5$ kOe for magnetization measurements.

Typical XRD pattern of the precursor is shown in Figure 1a. The peaks are perfectly consistent with the standard ones, JCPDS 34-1266. And all of them can be indexed to the tetragonal phase of FeOOH, or β-FeOOH as it is usually called. Figure 1b shows XRD pattern of the final product, which accords well with the standard one of magnetite. ICP-AES measurement was carried out to confirm the metal contents in the sample. The measured value of element Fe was 0.718, which is very near to the theoretical value of magnetite, 0.723, but not that of maghemite, 0.699. Hence it can be safely said that the final product is pure magnetite. After analysis of the XRD patterns and ICP-AES results, it comes to the conclusion that magnetite can be synthesized through reducing β-FeOOH with a somewhat weak reductant, hydrazine hydrate.

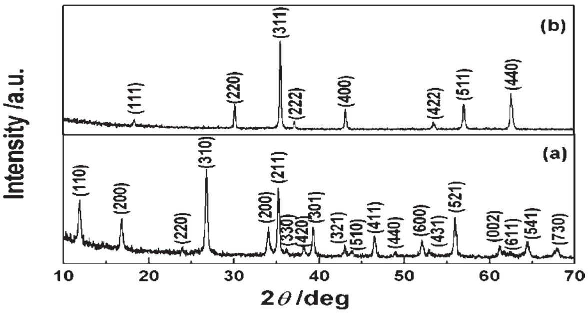

Figure 1. XRD patterns of the as-prepared samples: (a) β-FeOOH; (b) Fe_3O_4.

Figure 2 shows the TEM morphologies of as-prepared magnetite synthesized at 160 °C for 20 h. Large amounts of nanorods are found as well as cuboidal nanoparticles (Figure 2a).

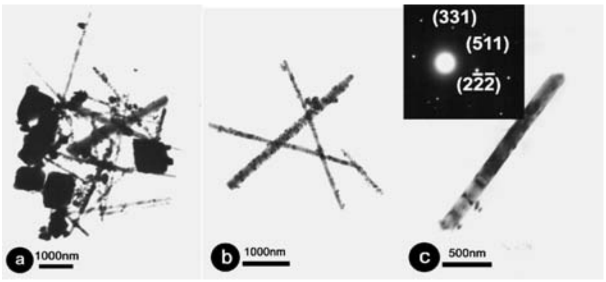

Figure 2. TEM images of magnetite synthesized at 160 °C for 20 h. (a) Nanorods together with nanoparticles; (b) nanorods of magnetite; (c) morphology of just on nanorod.

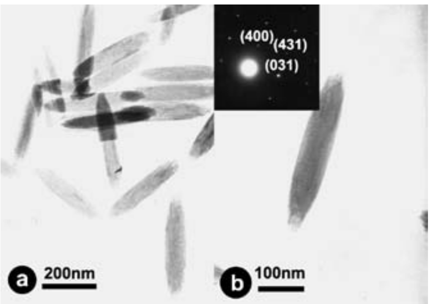

Figure 3. TEM images of β-FeOOH synthesized at 80 °C for 12 h. (a) Nanorods of β-FeOOH; (b) morphology of just one nanorod.

The β-FeOOH in our experiments was prepared according to the process described in ref 10. With this method, the morphology can be well controlled as uniform nanorods, as shown in Figure 3.

The ferric ions were forced to hydrolyze at the reaction temperature. The whole hydrothermal process can be depicted as follows:

$$\mathrm{Fe^{3+} + 6H_2O \rightarrow [Fe(H_2O)_6]^{3+}}$$

$$\mathrm{[Fe(H_2O)_6]^{3+} \rightarrow FeOOH + 4H_2O + 3H^+}$$

After the reductant was added and the temperature rose to the preset value, the reaction processed:

$$\mathrm{FeOOH + 2H_2O \rightarrow Fe(OH)_4{}^- + H^+}$$

$$\mathrm{4Fe(OH)_4{}^- + N_2H_4{\cdot}H_2O \rightarrow 4Fe(OH)_3{}^- + N_2\uparrow + 5H_2O}$$

$$\mathrm{2\ Fe(OH)_4{}^- + Fe(OH)_3{}^- \rightarrow Fe_3O_4 + 4H_2O + 3OH^-}$$

When the concentration of NaOH was 1 M, some of FeOOH would dissolved to form $\mathrm{Fe(OH)_4{}^-}$.[13] Under the effect of $\mathrm{N_2H_4{\cdot}H_2O}$, $\mathrm{Fe(OH)_4{}^-}$ was reduced to $\mathrm{Fe(OH)_3{}^-}$. And then the ferric and ferrous complex ions reacted to form magnetite.

With regards to the formation of the magnetite nanorods, there are two possible mechanisms, which are the direct reduction of the β-FeOOH and the dissolution–recrystallization process. After analysis of the TEM images, several details would be found, which may be helpful to make sure the formation mechanism.

First, it is clear that the cuboidal particles are grown by the dissolution–recrystallization process and that coexistence of two mechanisms in the same reaction seems unlikely. And cuboidal particles are found in Figure 2.

Second, because of the reason that crystal structure of β-FeOOH is quite different from that of magnetite, a direct reduction process would result in polycrystals. However, the SAED pattern (inset of Figure 2c) shows several clear spots, which is the characteristic of single crystals.

Third, if the magnetite nanorods were synthesized through a direct reduction, the size would be comparable with that of the precursor.[14] However, the former ones seem obviously larger either in length or in width.

On the basis of the facts mentioned above, it sounds reasonable to conclude that the reactions follow a dissolution–recrystallization mechanism.

At 160 °C, the rate of reduction is considerably slow. Large amounts of magnetites nucleate on β-FeOOH nanorods. What follows is the dissolution of β-FeOOH around the nucleus. Since the dissolution rate is slow, the reaction would proceed as in situ dissolution and in situ recrystallization. The whole β-FeOOH nanorods are finally converted into nanorods of magnetite. Meanwhile, a little amout of $\mathrm{Fe(OH)_4{}^-}$ and $\mathrm{Fe(OH)_3{}^-}$ existed in the solution reacts on their sufaces, which results in a much bigger morphology. At the same time, some magnetite nuclei also form in the solution and grow into well-crystallized cuboidal nanoparticles.

The magnetic properties of the as-prepared samples are shown in Figure 4. The hysteresis loops measured at room temperature exhibit a ferromagnetic character. Through the data in the figure, it can be known that the saturation magnetization is 81.7 emu/g, which is near to that of the related bulk ones (92 emu/g).[15]

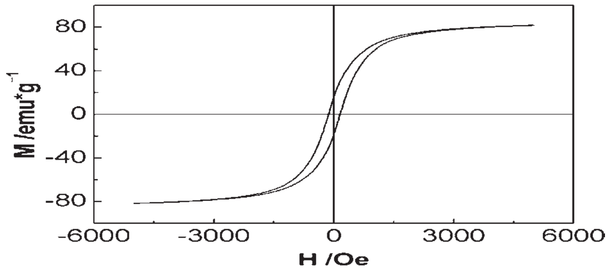

Figure 4. Magnetite hysteresis curves measured at room temperature for the final samples synthesized at 160 °C for 20 h.

In summary, magnetite nanorods were synthesized through reduction of β-FeOOH nanorods at 160 °C for 20 h, which proved the feasibility of our method. As to the growth mechanism, it was considered to be an in situ dissolution–recrystallization process. The magnetic properties of the samples were also studied. The high Ms value shows that the resulted magnetite nanorods are in good crystallization.

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References

1 Y. N. Xia, P. D. Yang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. Kim, and H. Q. Yan, *Adv. Mater.*, **15**, 353 (2003).
2 G. R. Patzke, F. Krumeich, and R. Nesper, *Angew. Chem., Int. Ed.*, **41**, 2446 (2002).
3 Z. L. Wang, *Adv. Mater.*, **15**, 432 (2003).
4 X. G. Peng, L. Manna, W. D. Yang, J. Wickham, E. Scher, A. Kadavanich, and A. P. Alivisatos, *Nature*, **404**, 59 (2000).
5 J. C. Bao, Y. Y. Liang, Z. Xu, and L. Si, *Adv. Mater.*, **15**, 1832 (2003).
6 S. Y. Lian, Z. H. Kang, E. B. Wang, M. Jiang, C. W. Hu, and L. Xu, *Solid State Commun.*, **127**, 605 (2003).
7 J. Wang, Z. M. Peng, Y. J. Huang, and Q. W. Chen, *J. Cryst. Growth*, **263**, 616 (2004).
8 J. Wang, Q. W. Chen, C. Zeng, and B. Y. Hou, *Adv. Mater.*, **16**, 137 (2004).
9 R. V. Kumar, Y. Koltypin, X. N. Xu, Y. Yeshurun, A. Gedanken, and I. Felner, *J. Appl. Phys.*, **89**, 6324 (2001).
10 X. Wang, X. Y. Chen, L. S. Gao, H. G. Zheng, M. R. Ji, C. M. Tang, T. Shen, and Z. D. Zhang, *J. Mater. Chem.*, **14**, 905 (2004).
11 C. X. Gao, Q. F. Liu, and D. S. Xue, *J. Mater. Sci. Lett.*, **21**, 1781 (2002).
12 Z. Y. Yuan and B. L. Su, *Chem. Phys. Lett.*, **381**, 710 (2003).
13 T. Ishikawa, Y. Kondo, A. Yasukawa, and K. Kandori, *Corros. Sci.*, **40**, 1239 (1998).
14 H. Itoh and T. Sugimoto, *J. Colloid Interface Sci.*, **265**, 283 (2003).
15 D. H. Han, J. P. Wang, and H. L. Luo, *J. Magn. Magn. Mater.*, **136**, 176 (1994).

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